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(54) CURABLE SILICONE COMPOSITION AND ITS CURED PRODUCT

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a curable silicone composition which rapidly cures, and after curing, forms a cured resin excellent in flexibility and adhesion.

SOLUTION: The curable silicone composition is characterized by comprising (A) an organopolysiloxane having at least two of epoxy group-containing monovalent hydrocarbon groups which do not have an aromatic ring, represented by a siloxane unit formula (1): $[R13SiO1/2]a[R22SiO2/2]b[R3SiO3/2]c$ (wherein R1, R2, and R3 are each a substituted or an unsubstituted monovalent hydrocarbon group, and at least two among those being the epoxy group-containing monovalent hydrocarbon groups which do not have the aromatic ring, R3 of ≥ 20 mol% being an aryl group; $a+b+c$ is 1, (a) being averagely $0 \leq a \leq 0.8$, (b) being averagely $0 \leq b \leq 0.8$, and (c) being averagely $0.2 \leq c \leq 1.0$), (B) a straight chain organopolysiloxane having at least two of phenolic hydroxy group-containing monovalent hydrocarbon groups, and (C) a curing accelerator.

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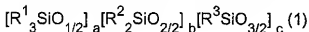
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CLAIMS

[Claim(s)]

[Claim 1]

(A) The following siloxane-units type (1) :



{R¹, R², and R³ are substitution or an unsubstituted monovalent hydrocarbon group among a formula, Before long, at least two pieces are epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring, more than 20 mol % of R³ is an aryl group, it is a+b+c=1, a is an average of 0<=a<=0.8, b is an average of 0<=b<=0.8, and c is an average of 0.2<=c<=1.0. }

Organopolysiloxane which has at least two epoxy group content monovalent hydrocarbon groups which come out and do not contain an aromatic ring expressed,

(B) organopolysiloxane of straight chain shape which has at least two phenolic hydroxyl group content monovalent hydrocarbon groups -- and

(C) A hardening accelerator

A hardenability silicone composition characterized by a thing, ** and others.

[Claim 2]

The hardenability silicone composition containing the (D) bulking agent according to claim 1.

[Claim 3]

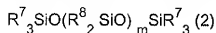
(A) The hardenability silicone composition according to claim 1 or 2, wherein an ingredient is liquefied.

[Claim 4]

(A) The hardenability silicone composition according to claim 1 or 2, wherein a is an average of 0<a<=0.8 among a siloxane-units type (1) showing an ingredient and b is 0.

[Claim 5]

(B) The hardenability silicone composition according to claim 1 or 2, wherein an ingredient is organopolysiloxane expressed with a following formula (2).



{R⁷ and R⁸ are same or different substitution or unsubstituted monovalent hydrocarbon groups (however, at least two pieces are phenolic hydroxyl group content monovalent hydrocarbon groups before long.) among a formula, and m is an integer of 0-1000. }

[Claim 6]

(A) The hardenability silicone composition according to claim 1 or 2 characterized by consisting of the (B) ingredient 1 - 1000 weight sections and the (C) ingredient 0.01 - 100 weight sections to Ingredient 100 weight section.

[Claim 7]

(A) The hardenability silicone composition according to claim 1 or 2, wherein an epoxy group of an ingredient is glycidoxy group or 3, and 4-epoxycyclohexyl group.

[Claim 8]

The hardenability silicone composition according to claim 1 or 2 which liquefied or is paste state.

[Claim 9]

A hardened material which hardens a hardenability silicone composition of a statement in any 1 paragraph of claims 1-8.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention is excellent in the hardening characteristic in detail about a hardenability silicone composition, and after hardening is related with the hardenability silicone composition used as the hardened material excellent in flexibility and an adhesive property.

[Background of the Invention]

[0002]

Conventionally, since the elastic modulus of the hardened material is greatly upright, as for hardenability resin compositions, such as an epoxy resin composition currently used for an electrical part, the electrical and electric equipment and the sealing agent for electronic devices, adhesives, etc., big stress is added to the electrical and electric equipment and electronic device closed by the thermal expansion of hardening resin by the resin. This stress causes the curvature of the electrical and electric equipment and an electronic device, and the curvature of a substrate, produces a crack in hardening resin itself, destroys the electrical and electric equipment and an electronic device, or produces a crevice between the electrical and electric equipment and an electronic device, and hardening resin.

[0003]

The hardenability resin composition which blends with hardening resin the silicone resin which has an epoxy group for the purpose of low-stress-izing of hardening resin (refer to JP,5-295084,A), the die attach paste (JP,10-147764,A.) which consists of a resultant of an epoxy resin and cyanate resin, and the dimethylsiloxane compound that has an epoxy group the die bonding material (JP,7-22441,A.) which consists of a reactant living thing of refer to JP,10-163232,A, epoxy group content silicone oil, and a phenol system organic compound JP,7-118365,A, referring to JP,10-130465,A, etc. are proposed. However, these hardened materials

are still upright, their low-stress-izing is insufficient, and there was a limit in application to the electrical and electric equipment and an electronic device.

[0004]

On the other hand, since the hardened material produced by hardening this is excellent in electrical properties, such as dielectric characteristics, volume resistivity, and electrical breakdown strength, the hardenability silicone composition is used for an electrical part, the electrical and electric equipment and the sealing agent for electronic devices, adhesives, etc. However, there was a problem that a hardenability silicone composition had a protection feature small [the coefficient of thermal expansion is large, or] to the protection ability of the electric electronic component, i.e., the shock from the outside, since intensity and the elastic modulus are low while the hardened material produced by hardening this is flexible. Since the adhesive property over the electrical and electric equipment and electronic device of a hardened material was low, the problem of producing a crevice was also between the electrical and electric equipment and an electronic device, and hardening resin. For this reason, although it was possible to blend a bulking agent and to make small the coefficient of thermal expansion of a flexible hardened material, the elastic modulus became large rapidly with combination of the bulking agent, there was a problem that that pliability and flexibility were lost, and there was a limit also in that improvement effect.

[0005]

The hardenability silicone resin composition with short gel time which consists of epoxy modified silicone oil and phenol modified silicone oil is proposed by JP,6-306084,A. However, the resin composition was inferior to hardenability, and there was a problem of requiring long cooking time in hardening of a constituent.

[0006]

[Patent documents 1] JP,5-295084,A

[Patent documents 2] JP,10-147764,A

[Patent documents 3] JP,10-163232,A

[Patent documents 4] JP,7-22441,A

[Patent documents 5] JP,7-118365,A

[Patent documents 6] JP,10-130465,A

[Patent documents 7] JP,6-306084,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0007]

This invention persons reached this invention, as a result of trying hard wholeheartedly, in order to solve the above-mentioned problem.

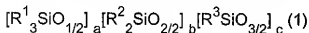
[0008]

That is, the purpose of this invention is hardened promptly and there is after hardening in providing the hardenability silicone composition used as hardening resin excellent in flexibility and an adhesive property.

[Means for Solving the Problem]

[0009]

This invention is the (A) following siloxane-units type (1). :

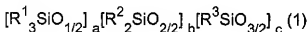


{ R^1 , R^2 , and R^3 are substitution or an unsubstituted monovalent hydrocarbon group among a formula, Before long, at least two pieces are epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring, more than 20 mol % of R^3 is an aryl group, it is $a+b+c=1$, a is an average of $0 \leq a \leq 0.8$, b is an average of $0 \leq b \leq 0.8$, and c is an average of $0.2 \leq c \leq 1.0$. Organopolysiloxane which has at least two epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring expressed with}, (B) It is related with a hardenability silicone composition consisting of organopolysiloxane of straight chain shape which has at least two phenolic hydroxyl group content monovalent hydrocarbon groups, and a (C) hardening accelerator.

[Effect of the Invention]

[0010]

The hardenability silicone composition of this invention is the (A) following siloxane-units type (1). :



{ R^1 , R^2 , and R^3 are substitution or an unsubstituted monovalent hydrocarbon group among a formula, Before long, at least two pieces are epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring, more than 20 mol % of R^3 is an aryl group, it is $a+b+c=1$, a is an average of $0 \leq a \leq 0.8$, b is an average of $0 \leq b \leq 0.8$, and c is an average of $0.2 \leq c \leq 1.0$. The organopolysiloxane which has at least two epoxy group content monovalent hydrocarbon groups which do not contain the aromatic ring expressed with}, (B) Since it consists of organopolysiloxane of the straight chain shape which has at least two phenolic hydroxyl group content monovalent hydrocarbon groups, and a (C) hardening accelerator, it hardens promptly and shortening of cooking time or reduction of heat cure temperature is attained in the forming cycle. That is, when it is used as a protective layer of detailed and vulnerable parts, the breakage can be prevented, and adhesion with a substrate also becomes firm from the ability of internal stress by thermal expansion to be made small in the forming cycle. The hardenability silicone composition of this invention shows a good adhesive property also to substrates of a difficulty adhesive property, such as a solder resist, nickel, and copper.

Therefore, it is useful as an electrical part, the encapsulant of an electronic device, a casting agent, a coating agent, adhesives, etc.

[Best Mode of Carrying Out the Invention]

[0011]

Hereafter, the hardenability silicone composition of this invention is explained in detail.

(A) An ingredient is base resin of this invention constituent, and the epoxy group reacts to the phenolic hydroxyl group in the (B) ingredient, constructs a bridge, and hardens it.

[0012]

(A) An ingredient is organopolysiloxane expressed with the following siloxane-units type (1),

$[R^3SiO_{3/2}]_a$ [whether it consists of units or it consists of $R^1_3SiO_{1/a} [2]$ unit, and $R^3SiO_{3/2}$ unit, and] $[R^2_2SiO_{2/2}]_b$ [whether it consists of a unit, and $R^3SiO_{3/2}$ unit, and] $[R^1_3SiO_{1/2}]_c$

Consisting of a unit, $R^2_2SiO_{2/2}$ unit, and $R^3SiO_{3/2}$ unit, molecular structure has reticulated or the shape of a three dimension.

$[R^1_3SiO_{1/2}]_a [R^2_2SiO_{2/2}]_b [R^3SiO_{3/2}]_c (1)$

R^1 , R^2 , and R^3 are substitution or an unsubstituted monovalent hydrocarbon group among a formula, and at least two pieces are epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring. In an epoxy group content monovalent hydrocarbon group, it is required not to contain an aromatic ring. This is because this invention constituent stops hardening promptly when an aromatic ring is contained in an epoxy group content monovalent hydrocarbon group.

[0013]

As substitution or unsubstituted monovalent hydrocarbon groups other than the epoxy group content monovalent hydrocarbon group which does not contain an aromatic ring, it is preferred that it is substitution or an unsubstituted monovalent hydrocarbon group with 1-20 carbon atoms, and specifically, Alkyl groups, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, a propyl group, a butyl group, and a pentyl group, a tolyl group, and a xylyl group, and a phenethyl group; halogenation alkyl groups, such as a chloromethyl group and a 3,3,3-trifluoropropyl group, are illustrated. Especially, an alkyl group, especially a methyl group are preferred. As an epoxy group content monovalent hydrocarbon group which does not contain an aromatic ring, 2-glycidoxy ethyl group, 3-glycidoxy propyl group, 4-glycidoxybutyl group, 2-(3,4-epoxycyclohexyl) ethyl group, 3-(3,4-epoxycyclohexyl) propyl group, 2-(3,4-epoxy NORUBORUNENIRU) ethyl group, 2-(3,4-epoxy-3-methylcyclohexyl) The epoxy group joint alkyl group of a-2-methylethyl group etc. is illustrated. Especially, 3-glycidoxy propyl group and 2-(3,4-epoxycyclohexyl) ethyl group are preferred. Two or more epoxy group content monovalent hydrocarbon groups which do not

contain these aromatic rings exist in 1 intramolecular. (A) It is preferred that it is the range of 100-2000, they are 100-1000 more preferably, and the weight per epoxy equivalents (numerical value which divided the weight average molecular weight of the (A) ingredient by the number of the epoxy groups in one molecule of (A) ingredients) of an ingredient are 100-700 most preferably. In less than the minimum of this range, this is because there is a case where the flexibility of the hardened material of this invention constituent becomes less enough, and is because the adhesive property of this invention constituent and hardenability may get worse or the hardened material of this invention constituent may become very weak, if the maximum of this range is exceeded.

[0014]

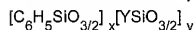
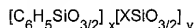
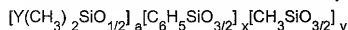
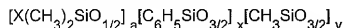
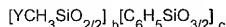
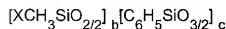
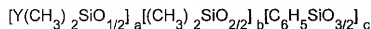
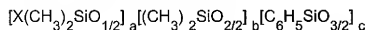
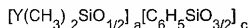
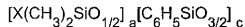
As for more than 20 mol % of R^3 , it is preferred that it is an aryl group and more than 50 mol % is an aryl group, and it is more preferred that more than 80 mol % is an aryl group. This is because neither compatibility with the (B) ingredient nor an adhesive property with a substrate may be enough in it being less than a mentioned range or the intensity of the hardened material of this invention hardenability silicone composition may not be enough. Especially as an aryl group of R^3 , a phenyl group is preferred. a, b, and c mean the number of average mols at the time of setting the number of sum total mols of each siloxane units to 1. Therefore, it is $a+b+c=1$. It is preferred that it is $a+b \neq 0$. This is because the viscosity may become high too much, it may be dealt with and workability may get worse, if the (A) ingredient consists only of $R^3SiO_{3/2}$ unit. a is an average of $0 < a \leq 0.8$, is $0 < a \leq 0.6$ preferably, and is $0.3 < a \leq 0.6$ more preferably. This is because the molecular weight of organopolysiloxane may become small too much, the (A) ingredient may ooze out from the hardened material of this invention constituent and the circumference may be polluted, if the maximum of this range is exceeded. b is an average of $0 < b \leq 0.8$, and is $0 < b \leq 0.6$ preferably. This is because the hardened material of this invention constituent may become weak if b exceeds the maximum of this range. c is an average of $0.2 \leq c \leq 1.0$, and is $0.4 \leq c \leq 1.0$ preferably. The adhesive property of this invention constituent becomes less enough [this] in c being less than the minimum of this range, and. It is because viscosity becomes high too much, and the handling workability of this invention constituent gets worse or there is a case where the flexibility of that hardened material becomes less suitable, when this invention hardened material may become weak and exceeds the maximum of this range.

[0015]

The organopolysiloxane shown with a following formula is illustrated as a desirable (A) ingredient expressed with a siloxane-units type (1). Among each of following formulas, although a, b, and c are as aforementioned, a and b are not 0. x and y are $0.2 \leq x \leq 1.0$ and $0 < y < 0.2$, and are $x+y=c$. X express a glycidoxy propyl group among a following formula, and Y

expresses 2-(3,4-epoxycyclohexyl) ethyl group.

[0016]



[0017]

(A) The alkoxysilane which has an epoxy group content monovalent hydrocarbon group which does not contain phenyl trialkoxysilane and an aromatic ring as a method of preparing an ingredient, For example, By the dealcoholization condensation reaction of 3-glycidoxypropyltrimethoxysilane or 2-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane. the alkoxysilane which has a silanol group in the branched state phenylpolyorganosiloxane prepared by the cohydrolysis condensation reaction of method; phenyltrichlorosilane or phenyl trialkoxysilane to prepare, and an epoxy group content monovalent hydrocarbon group which does not contain an aromatic ring -- for example, How to prepare by a dealcoholization condensation reaction with 3-glycidoxypropyltrimethoxysilane or 2-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane; It reaches, The silicon atom absorbed water matter atom content organopolysiloxane prepared by carrying out the cohydrolysis condensation reaction of phenyltrichlorosilane or the phenyl trialkoxysilane under silicon atom absorbed water matter atom content Silang existence, such as dimethylchlorosilane, The method of preparing by a hydrosilylation reaction with the compound which has an epoxy group content monovalent hydrocarbon group which does not contain an aliphatic unsaturated group and an aromatic ring is illustrated.

[0018]

Otherwise, By the cohydrolysis condensation reaction of phenyltrichlorosilane or phenyl trialkoxysilane. The prepared branched state phenyl organopolysiloxane. Chain both-ends trimethylsiloxy group blockade methyl. (3-glycidoxy propyl) A siloxane dimethylsiloxane copolymer or a chain both-ends trimethylsiloxy group blockade methyl (2-(3,4-

epoxycyclohexyl) ethyl siloxane) dimethylsiloxane copolymer. Silicone resin, annular methyl (3-glycidoxy propyl) siloxane, or annular methyl(2- (3,4-epoxycyclohexyl)) ethyl siloxane which consists of a method; $[C_6H_5SiO_{3/2}]$ unit which carries out equilibrium polymerization under existence of a basic polymerization catalyst. How to carry out equilibrium polymerization under existence of a basic polymerization catalyst; It reaches, $[C_6H_5SiO_{3/2}]$ silicone resin, the annular methyl (3-glycidoxy propyl) siloxane or the annular methyl (2-(3,4-epoxycyclohexyl) ethyl) siloxane, and annular dimethylsiloxane which consist of units. The method of carrying out equilibrium polymerization under acidity or existence of a basic polymerization catalyst is also illustrated.

[0019]

(A) One kind of organopolysiloxane may be sufficient as an ingredient, and the mixture which consists of two or more kinds of organopolysiloxane may be sufficient as it. The description at 25 ** may be any of a liquid and a solid state. It is mixable to other ingredients and homogeneity by using an organic solvent in the case of a solid state, or heating. It is preferred from the ease of combination or handling that it is a fluid at 25 **. (A) As for the weight average molecular weight of an ingredient, 500-10000 are preferred, and 750-3000 are more preferred.

[0020]

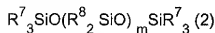
(A) The hydroxyl group in which an ingredient originates in the manufacturing method; a small amount of hydrolytic bases, such as an alkoxy group and an acetoxy group, may be contained.

[0021]

(B) Organopolysiloxane of the straight chain shape containing at least two phenolic hydroxyl group content monovalent hydrocarbon groups is a cross linking agent of the (A) ingredient, and there is work which reacts to the epoxy group in the (A) ingredient by operation of the (C) ingredient mentioned later, and carries out bridge construction hardening of this invention constituent. (B) As substitution or unsubstituted monovalent hydrocarbon groups other than the phenolic hydroxyl group content monovalent hydrocarbon group in an ingredient, there are an alkyl group, an aryl group, an aralkyl group, and a halogenation alkyl group. (B) An ingredient may contain a small number of silicon bond hydrogen atom, a hydroxyl group, and an alkoxy group. (B) Although solid and liquefied any may be sufficient as an ingredient in 25 **, the shape of the ease of handling to liquid is preferred. It is specifically preferred to have the viscosity of 1 - 1 million mPa-s in 25 **, and it is preferred especially that it is within the limits of 100 - 5000 mPa-s. This is because there is a tendency for the flexibility of a hardened material and mechanical strength which are produced by hardening this constituent as it is less than the minimum of a mentioned range to fall, and is because there is a tendency for the handling workability of this invention constituent to fall, on the other hand when the maximum of a mentioned range is exceeded.

[0022]

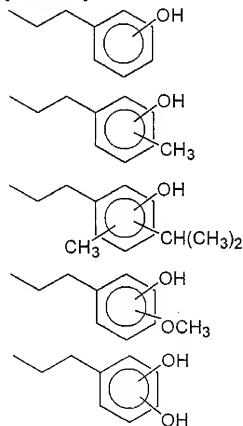
The desirable (B) ingredient is expressed with a following formula (2). This is because it becomes advantageous to raising the flexibility of the hardened material of this invention constituent.



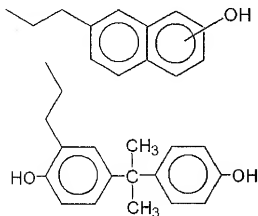
or [that the inside of a formula, R^7 , and R^8 are the same] -- or it is different substitution or unsubstituted monovalent hydrocarbon group, and at least two pieces are phenolic hydroxyl group content monovalent hydrocarbon groups among these. Although the phenolic hydroxyl group content monovalent hydrocarbon group should just be in [two or more] a molecule, they are two pieces preferably. A desirable phenolic hydroxyl group content monovalent hydrocarbon group is a phenolic group joint alkyl group, and the following are illustrated.

[0023]

[Formula 1]



[Formula 2]



[0024]

As other substitution or unsubstituted monovalent hydrocarbon groups, A methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, Alkyl groups, such as a heptyl group; Aryl group; benzyls, such as a phenyl group, a tolyl group, a xylyl group, and a naphthyl group, Aralkyl groups, such as a phenethyl group; alkyl halide groups, such as alkenyl group; chloromethyl groups, such as a vinyl group, an allyl group, a butenyl group, a PETENIRU group, and a hexenyl group, 3-chloropropyl group, and a 3,3,3-trifluoropropyl group, are illustrated. An alkyl group, especially a methyl group are especially preferred. m in a formula is an integer of 0-1000, is 0-100 preferably, and is 0-20 more preferably. It is because this has the low viscosity of the (B) ingredient enough in m in a formula being in a mentioned range, and combination for the (A) ingredient and handling become easy and it becomes still more possible to make the hardenability silicone composition of this invention liquefied with a non-solvent.

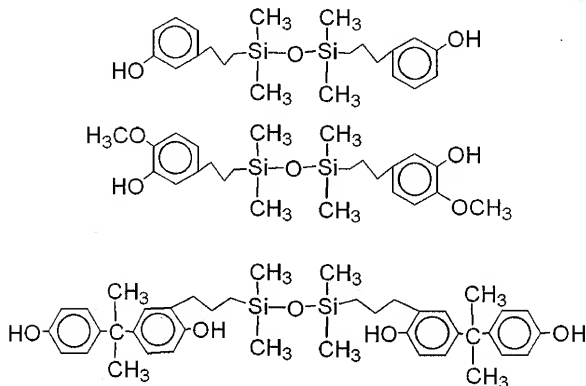
[0025]

(B) They are a quantity from which a mole ratio of a phenolic hydroxyl group in the (B) ingredient is set to 0.2-5 to an epoxy group in the (A) ingredient, loadings of an ingredient have a preferred quantity especially set to 0.3-2.5, and its quantity used as 0.8-1.5 is more preferred. This is for a mechanical property after hardening to fall remarkably, if a constituent does not fully harden that a mole ratio of a phenolic hydroxyl group in the (B) ingredient to an epoxy group in the (A) ingredient is less than 0.2 and 5 is exceeded.

[0026]

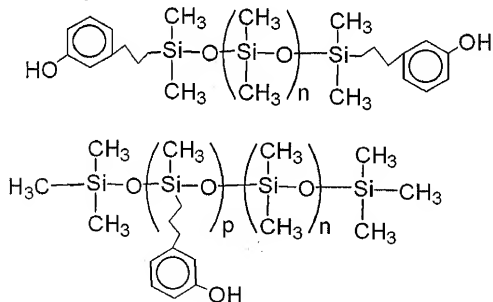
The following are illustrated as a desirable (B) ingredient. n in a formula is an integer of 1-20, and p is an integer of 2-10.

[Formula 3]



[0027]

[Formula 4]



[0028]

(B) An ingredient can be prepared by a publicly known method. For example, the method of carrying out the addition reaction of an alkenyl group content phenolic compound and the

organopolysiloxane which has a silicon atom absorbed water matter atom under existence of a hydrosilylation catalyst is illustrated.

[0029]

(C) An ingredient is an ingredient for promoting a reaction of an epoxy group in the (A) ingredient, and a phenolic hydroxyl group in the (B) ingredient, i.e., hardening of this invention constituent. (C) As an ingredient, organophosphorus compounds, such as organic metallic compounds, such as the third class amine compound, aluminum, and a zirconium, and phosphine, a different ring type amine compound, a boron complex compound, organic ammonium salt, organic sulfonium salt, organic peroxide, these reactants, etc. are illustrated. For example, triphenyl phosphine, tributyl phosphine, Tri (p-methylphenyl) phosphine, The Tri (nonylphenyl) phosphine, triphenylphosphine triphenyl borate, The Lynn system compounds, such as tetraphenylphosphine tetraphenyl borate; Triethylamine, Benzyldimethylamine, alpha-methylbenzyl dimethylamine, 1, a tertiary amine compound of 8-diazabicyclo [5.4.0] undecene 7 grade; 2-methylimidazole, Imidazole compounds, such as 2-phenylimidazole and 2-phenyl-4-methylimidazole, are illustrated. Since working life of a hardenability silicone composition of this invention can be extended, an encapsulated hardening accelerator is preferred. As an encapsulated hardening accelerator, an encapsulation amine catalyst (HX-3088: made by Asahi Chemical Co., Ltd.) which blended an amine catalyst into a bisphenol A type epoxy resin is mentioned.

[0030]

(C) If an ingredient is sufficient quantity to stiffen this invention constituent, although the loadings are not limited, it is 0.01 per (A) ingredient 100 weight section - 100 weight section, and still more preferably, they are 0.01 - 50 weight section, and are 0.1 - 5 weight section most preferably.

[0031]

In order to raise intensity of a hardened material, the (D) bulking agent may be blended with this invention constituent. Ceramic fiber which uses glass fiber, an alumina fiber, alumina, and silica as an ingredient as a bulking agent, Fibrous fillers, such as a boron fiber, a zirconia fiber, silicon carbide fiber, and a metal fiber; Fused silica, Crystalline silica, precipitation silica, fumed silica, pyrogenic silica, a zinc oxide, Calcination clay, carbon black, a glass bead, alumina, talc, Calcium carbonate, clay, aluminium hydroxide, magnesium hydroxide, Particulate matter-like bulking agent [, such as barium sulfate, aluminium nitride, boron nitride, silicon carbide, an aluminum oxide, magnesium oxide, titanium oxide, beryllium oxide, kaolin, mica, and zirconia,]; and two or more sorts of these mixtures are illustrated. Although mean particle diameter or shape of the (D) ingredient are not limited, since a moldability is excellent, spherical silica whose mean particle diameter is 0.1-40 micrometers is preferred.

[0032]

(D) Since loadings of an ingredient do not spoil the mobility of this invention constituent, its 0 - 2000 weight section is preferred to a total of 100 weight sections of the (A) ingredient and the (B) ingredient, and its 50 - 1000 weight section is still more preferred.

[0033]

In order to make the (A) ingredient, the (B) ingredients, or those mixtures distribute the (D) ingredient good and to raise an adhesive property to a substrate at the time of hardening of this invention constituent, coupling agents, such as a silane coupling agent and a titanate coupling agent, may be blended. As a silane coupling agent, 3-glycidoxypropyltrimethoxysilane, Epoxy group content alkoxysilane;N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, such as 3-glycidoxy propyl methyldiethoxysilane and 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, Sulfhydryl group content alkoxysilane, such as amino group content alkoxysilane;3-mercapto propyltrimethoxysilane, such as 3-aminopropyl triethoxysilane and N-phenyl-3-aminopropyl trimethoxysilane, is illustrated. i-propoxy CHITANTORI (i-isostearate) is illustrated as a titanate coupling agent.

[0034]

As arbitrary ingredients, in addition, a tetramethoxy silane, a tetraethoxysilane, Dimethyldimethoxysilane, methylphenyl dimethoxysilane, methylphenyl diethoxysilane, Phenyltrimethoxysilane, methyl trimethoxysilane, methyl triethoxysilane, Alkoxysilane, such as vinyltrimethoxysilane, allyl trimethoxysilane, and allyl triethoxysilane; Hexane, Organic solvents, such as ketones, such as aromatic solvents, such as aliphatic series system solvents, such as heptane, toluene, and xylene, methyl ethyl ketone, and methyl isobutyl ketone, may be blended.

[0035]

A hardenability silicone composition of this invention is obtained by mixing the (D) ingredient and other optional components uniformly by the (A) ingredient, the (B) ingredient, the (C) ingredient, and necessity. Although a mixing method in particular is not limited, the (A) ingredient, the (B) ingredient, the (C) ingredient, After carrying out the premix of a method; (A) ingredient and (B) ingredient which blend the (D) ingredient and other optional components simultaneously as occasion demands, (C) After carrying out the premix of the (D) ingredient or the other optional components to a method; (A) ingredient which blends the (D) ingredient and other optional components with an ingredient as occasion demands, and the (B) ingredient as occasion demands, a method of blending the (C) ingredient is illustrated. (A) There is no limitation especially as a mixed device which mixes the (D) ingredient and other optional components by ingredient, the (B) ingredient, the (C) ingredient, and necessity, A continuous mixer of one axis or two axes, 2 rolls, a loss mixer, the Hobart mixer, a dental mixer, a planetary mixer, and a kneader mixer are illustrated.

[0036]

A hardenability silicone composition of this invention can be used by methods, such as a transfer mold, injection molding, potting, casting, powder coating, dip coating, and dropping. It is preferred that liquefied or it is paste state from being able to choose various directions for use, such as potting, screen-stencil, spreading, and being easy to suit a use of small-quantity use. Since after hardening becomes the hardened material excellent in flexibility and an adhesive property, a hardenability silicone composition of this invention is useful as an electrical part, encapsulant of an electronic device, a casting agent, a coating agent, adhesives, etc.

[Example]

[0037]

Hereafter, an example explains this invention. The various characteristics of the hardenability silicone composition and the hardened material were measured by the method shown below.

[0038]

[Viscosity] It measured on condition of for 25 ** and 2.5/ of number of rotations using :E type viscosity meter (the product made by TOKIMEC, a DIGITAL VISCOMETER DV-U-E II type).

[Coefficient of thermal expansion]: After filling up with the hardenability silicone composition the metallic mold which has a cavity 4 mm in width, 15 mm in length, and 4 mm in depth and defoaming by 70mmHg, press hardening was carried out for 60 minutes on condition of 150 ** and 2.5MPa. Subsequently, the 2nd order was heated in 2-hour oven at 180 **, and the hardened material specimen was obtained. TMA (TM-9200 by vacuum science-and-engineering stock meeting incorporated company) was used, temperature up of the obtained specimen was carried out from 25 ** to 210 ** by a part for 2.5 ** of temperature-up/, and thermal expansion was measured.

[The rate of complex viscoelasticity]: After filling up with the hardenability silicone composition the metallic mold which has a cavity 10 mm in width, 50 mm in length, and 2 mm in depth and defoaming by 70mmHg, press hardening was carried out for 60 minutes on condition of 150 ** and 2.5MPa. Subsequently, the hardened material specimen heated the 2nd order in 2-hour oven at 180 ** was obtained. The rate of complex viscoelasticity in 25 ** when an ARES viscoelasticity measuring apparatus (made by Rheometric Scientific) is used and temperature up of the obtained specimen is carried out from -50 ** to 150 ** by a part for 0.5% of torsion, pitch [of 1 Hz], and heating-rate/ of 3 ** was measured.

[Adhesive property] : A solder resist (the developed type solder resist of negatives, Taiyo Ink Mfg., Inc. make PSR-4000 CC02/CA-40 CC02) is applied to the base made of bismaleimide triazine resin (common name: BT resin), ultraviolet drying – it exposed and hardened (150 **, 1 hour), the solder resist layer (50-micrometer thickness) was formed on BT board, and this was made into adherend. In addition, the glass plate, the aluminum board, the nickel board, and the copper plate were also evaluated as adherend. After applying about 1 cm of

hardenability silicone composition ³ on such adherends and heating it in 2-hour oven at 125 **, oven heating was performed at 180 ** for 2 hours, and the specimen for adhesive evaluation was obtained. From the obtained specimen, visual observation of peel-off and its adhesive property was carried out for the hardened material under the microscope using the dental spatula. The case of ** and interfacial peeling was made into x for the case where interfacial peeling of the case of cohesive failure is carried out after O and a pellicle have remained. [Hardenability examination]: The 40-micrometer-thick tape was stuck five sheets on the glass plate, the cavity (15 mm in width, 50 mm in length, and 0.2 mm in thickness) was provided, and it was used and filled up with the hardenability silicone composition for the squeegee. The obtained specimen was put into 150 ** hot wind circle method oven, the dental spatula described the hardenability silicone composition surface every 15 minutes, and time until the cobwebbing of a sample is lost was pursued.

[Weight average molecular weight]: The weight average molecular weight which measured toluene by the solvent and GPC and which carried out polystyrene conversion is shown.

[0039]

[Example 1]

The weight average molecular weight 1000, viscosity 9630 mPa-s which are expressed with the following siloxane-units type (3), They are 13.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (3).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 25.0 weight sections and the following siloxane-units type (4) in organopolysiloxane of the weight per epoxy equivalent 345. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 1.0 weight sections and 60.0 weight sections of spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) were mixed for HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd., amine-catalyst content: 40 % of the weight), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.

$[X(CH_3)_2SiO_{1/2}]C_6H_5SiO_{3/0.4}^{12}]_{0.6} \quad (3)$

(X in a formula is 3-glycidoxy propyl group)

$Z-(CH_3)_2SiO(CH_3)_2Si-Z \quad (4)$

(The inside Z of a formula is 3-(m-hydroxyphenyl) propyl group)

[0040]

[Example 2]

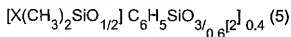
The weight average molecular weight 1000, viscosity 9630 mPa-s which are expressed with

said formula (3), They are 13.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (3).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 25.0 weight sections and said formula (4) in organopolysiloxane of the weight per epoxy equivalent 345. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 3-glycidoxypropyltrimetoxysilane -- 1.0 weight sections and HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd..) Amine-catalyst content: 1.0 weight sections and 60.0 weight sections of spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) were mixed for 40 % of the weight, and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.

[0041]

[Example 3]

The weight average molecular weight 1000, viscosity 1290 mPa-s which are expressed with the following siloxane-units type (5), They are 17.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (5).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 21.0 weight sections and said formula (4) in organopolysiloxane of the weight per epoxy equivalent 270. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 3-glycidoxypropyltrimetoxysilane -- 1.0 weight sections and HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd..) Amine-catalyst content: 1.0 weight sections were mixed for 40 % of the weight, 60.0 weight sections were mixed for spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.



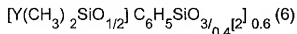
(X in a formula is 3-glycidoxy propyl group)

[0042]

[Example 4]

The weight average molecular weight 2200, viscosity 1900 mPa-s which are expressed with the following siloxane-units type (6), They are 14 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (6).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 24 weight sections and said

formula (4) in organopolysiloxane of the weight per epoxy equivalent 345. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 3-glycidoxypropyltrimetoxysilane -- 1.0 weight sections and HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections and 60.0 weight sections of spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) were mixed for 40 % of the weight, and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.



(The inside Y of a formula is 2-(3,4-epoxycyclohexyl) ethyl group)

[0043]

[Comparative example 1]

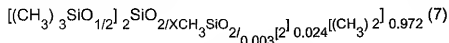
bisphenol A type liquid epoxy resin (Japan epoxy resin incorporated company make.) Epicoat 828, viscosity 15 mPa-s, and the weight per epoxy equivalent 190 23.0 weight sections, A liquefied phenol compound (made in Meiwa Chemicals, Inc., MEH8000H) 17.0 weight sections, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections and spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) 60.0 weight section were mixed for 40 % of the weight, and the hardenability epoxy resin composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 2. It was admitted that the complex modulus of the hardened material was very highly [as 2900] upright.

[0044]

[Comparative example 2]

The weight average molecular weight 45000, viscosity 17700 mPa-s which are expressed with the following siloxane-units type (7), Organopolysiloxane of the weight per epoxy equivalent 3850 36.0 weight sections, They are 2.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (7).) about organopolysiloxane of viscosity 3050 mPa-s expressed with said formula (4). The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections were mixed for 40 % of the weight, 60.0 weight sections were mixed for spherical amorphous silica

(ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 2.

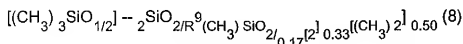


(X in a formula is 3-glycidioxy propyl group)

[0045]

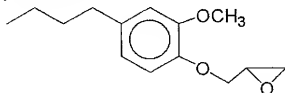
[Comparative example 3]

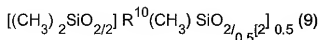
The weight average molecular weight 1500, viscosity 1200 mPa-s which are expressed with the following siloxane-units type (8), Organopolysiloxane of the weight per epoxy equivalent 370 21.0 weight sections, They are 17.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (8).) about organopolysiloxane of the weight average molecular weight 630 and viscosity 840 mPa-s which are expressed with the following siloxane-units type (9). The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (9) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd..) An encapsulation amine catalyst content 40% of the weight in bisphenol A type liquid epoxy resin 1.0 weight sections, 1.0 weight sections and spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) 70.0 weight section were mixed for 3-glycidioxypropyltrimetoxysilane, and the hardenability silicone composition was prepared. The coefficient of thermal expansion and the rate of complex viscoelasticity were investigated on condition of the above-mentioned after vacuum defoaming except having carried out oven heating at 180 ** for 2 hours, after carrying out casting to the metallic mold and carrying out oven heating at 150 ** for 2 hours. An adhesive property and cure time were investigated on condition of the above-mentioned. The characteristic is shown in Table 2.



Basis as which R^9 in a formula is expressed in a lower type :

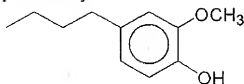
[Formula 5]





Basis as which R^{10} in a formula is expressed in a lower type :

[Formula 6]

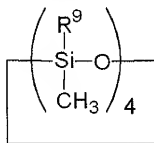


[0046]

[Comparative example 4]

The weight average molecular weight 950, viscosity 177000 mPa-s which are expressed with a lower type (10), They are 22.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (10).) about organopolysiloxane of the weight average molecular weight 630 and viscosity 840 mPa-s which are expressed with 16.0 weight sections and the above-mentioned formula (9) in organopolysiloxane of the weight per epoxy equivalent 240. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with said formula (9) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd..) An encapsulation amine catalyst content 40% of the weight in bisphenol A type liquid epoxy resin 1.0 weight sections, 1.0 weight sections and spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) 70.0 weight section were mixed for 3-glycidoxypyrtrimetoxysilane, and the hardenability silicone composition was prepared. The coefficient of thermal expansion and the rate of complex viscoelasticity were investigated on condition of the above-mentioned after vacuum defoaming except having carried out oven heating at 180 ** for 2 hours, after carrying out casting to the metallic mold and carrying out oven heating at 150 ** for 2 hours. An adhesive property and cure time were investigated on condition of the above-mentioned. The characteristic is shown in Table 2.

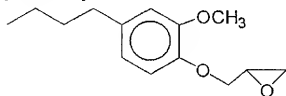
[Formula 7]



(10)

Basis as which R^9 in a formula is expressed in a lower type :

[Formula 8]

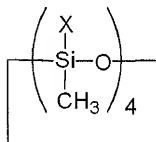


[0047]

[Comparative example 5]

The weight average molecular weight 696, viscosity 110 mPa·s which are expressed with a lower type (11), They are 20.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (11).) about organopolysiloxane of viscosity 3050 mPa·s expressed with 17.0 weight sections and said formula (4) in organopolysiloxane of the weight per epoxy equivalent 174. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections were mixed for 40 % of the weight, 60.0 weight sections were mixed for spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 2.

[Formula 9]



(1 1)

(X in a formula is 3-glycidioxy propyl group)

[0048]

[Table 1]

		実施例 1	実施例 2	実施例 3	実施例 4
粘度	(Pa·s)	10	14	7	15
熱膨張率	(ppm/°C)	110	110	120	100
複素粘弾性率	(MPa)	80	86	90	90
接着性	(ソルダーレス)	○	○	○	○
接着性	(ニッケル)	○	○	○	○
接着性	(銅)	○	○	○	○
接着性	(アルミニウム)	○	○	○	○
接着性	(ガラス)	○	○	○	○
硬化時間	(min)	15	15	15	15

[0049]

[Table 2]

		比較例 1	比較例 2	比較例 3	比較例 4	比較例 5
粘度	(Pa·s)	199	>500	27	81	5
熱膨張率	(ppm/°C)	67	—*	130	80	120
複素粘弾性率	(MPa)	2900	—*	60	350	80
接着性	(ソルダーレス)	○	×	○	○	×
接着性	(ニッケル)	○	×	○	○	×
接着性	(銅)	○	×	○	○	×
接着性	(アルミニウム)	○	×	○	○	○
接着性	(ガラス)	○	×	○	○	○
硬化時間	(min)	30	90	120	120	15

*: the hardened material was dramatically weak and was not able to measure.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]

[0001]

This invention is excellent in the hardening characteristic in detail about a hardenability silicone composition, and after hardening is related with the hardenability silicone composition used as the hardened material excellent in flexibility and an adhesive property.

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PRIOR ART

[Background of the Invention]

[0002]

Conventionally, since the elastic modulus of the hardened material is greatly upright, as for hardenability resin compositions, such as an epoxy resin composition currently used for an electrical part, the electrical and electric equipment and the sealing agent for electronic devices, adhesives, etc., big stress is added to the electrical and electric equipment and electronic device closed by the thermal expansion of hardening resin by the resin. This stress causes the curvature of the electrical and electric equipment and an electronic device, and the curvature of a substrate, produces a crack in hardening resin itself, destroys the electrical and electric equipment and an electronic device, or produces a crevice between the electrical and electric equipment and an electronic device, and hardening resin.

[0003]

The hardenability resin composition which blends with hardening resin the silicone resin which has an epoxy group for the purpose of low-stress-izing of hardening resin (refer to JP,5-295084,A), the die attach paste (JP,10-147764,A.) which consists of a resultant of an epoxy resin and cyanate resin, and the dimethylsiloxane compound that has an epoxy group the die bonding material (JP,7-22441,A.) which consists of a reactant living thing of refer to JP,10-163232,A, epoxy group content silicone oil, and a phenol system organic compound JP,7-118365,A, referring to JP,10-130465,A, etc. are proposed. However, these hardened materials are still upright, their low-stress-izing is insufficient, and there was a limit in application to the electrical and electric equipment and an electronic device.

[0004]

On the other hand, since the hardened material produced by hardening this is excellent in electrical properties, such as dielectric characteristics, volume resistivity, and electrical breakdown strength, the hardenability silicone composition is used for an electrical part, the

electrical and electric equipment and the sealing agent for electronic devices, adhesives, etc. However, there was a problem that a hardenability silicone composition had a protection feature small [the coefficient of thermal expansion is large, or] to the protection ability of the electric electronic component, i.e., the shock from the outside, since intensity and the elastic modulus are low while the hardened material produced by hardening this is flexible. Since the adhesive property over the electrical and electric equipment and electronic device of a hardened material was low, the problem of producing a crevice was also between the electrical and electric equipment and an electronic device, and hardening resin. For this reason, although it was possible to blend a bulking agent and to make small the coefficient of thermal expansion of a flexible hardened material, the elastic modulus became large rapidly with combination of the bulking agent, there was a problem that that pliability and flexibility were lost, and there was a limit also in that improvement effect.

[0005]

The hardenability silicone resin composition with short gel time which consists of epoxy modified silicone oil and phenol modified silicone oil is proposed by JP,6-306084,A. However, the resin composition was inferior to hardenability, and there was a problem of requiring long cooking time in hardening of a constituent.

[0006]

[Patent documents 1] JP,5-295084,A

[Patent documents 2] JP,10-147764,A

[Patent documents 3] JP,10-163232,A

[Patent documents 4] JP,7-22441,A

[Patent documents 5] JP,7-118365,A

[Patent documents 6] JP,10-130465,A

[Patent documents 7] JP,6-306084,A

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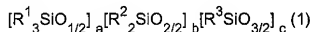
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EFFECT OF THE INVENTION

[Effect of the Invention]

[0010]

The hardenability silicone composition of this invention is the (A) following siloxane-units type (1). :



{R¹, R², and R³ are substitution or an unsubstituted monovalent hydrocarbon group among a formula, Before long, at least two pieces are epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring, more than 20 mol % of R³ is an aryl group, it is a+b+c=1, a is an average of 0<=a<=0.8, b is an average of 0<=b<=0.8, and c is an average of 0.2<=c<=1.0. The organopolysiloxane which has at least two epoxy group content monovalent hydrocarbon groups which do not contain the aromatic ring expressed with), (B) Since it consists of organopolysiloxane of the straight chain shape which has at least two phenolic hydroxyl group content monovalent hydrocarbon groups, and a (C) hardening accelerator, it hardens promptly and shortening of cooking time or reduction of heat cure temperature is attained in the forming cycle. That is, when it is used as a protective layer of detailed and vulnerable parts, the breakage can be prevented, and adhesion with a substrate also becomes firm from the ability of internal stress by thermal expansion to be made small in the forming cycle. The hardenability silicone composition of this invention shows a good adhesive property also to substrates of a difficulty adhesive property, such as a solder resist, nickel, and copper. Therefore, it is useful as an electrical part, the encapsulant of an electronic device, a casting agent, a coating agent, adhesives, etc.

[Translation done.]

* NOTICES *

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- 3.In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]

[0007]

This invention persons reached this invention, as a result of trying hard wholeheartedly, in order to solve the above-mentioned problem.

[0008]

That is, the purpose of this invention is hardened promptly and there is after hardening in providing the hardenability silicone composition used as hardening resin excellent in flexibility and an adhesive property.

[Translation done.]

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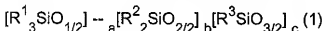
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MEANS

[Means for Solving the Problem]

[0009]

This invention is the (A) following siloxane-units type (1). :



{R¹, R², and R³ are substitution or an unsubstituted monovalent hydrocarbon group among a formula, Before long, at least two pieces are epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring, more than 20 mol % of R³ is an aryl group, it is a+b+c=1, a is an average of 0<=a<=0.8, b is an average of 0<=b<=0.8, and c is an average of 0.2<=c<=1.0. Organopolysiloxane which has at least two epoxy group content monovalent hydrocarbon groups which do not contain an aromatic ring expressed with}, (B) It is related with a hardenability silicone composition consisting of organopolysiloxane of straight chain shape which has at least two phenolic hydroxyl group content monovalent hydrocarbon groups, and a (C) hardening accelerator.

[Translation done.]

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EXAMPLE

[Example]

[0037]

Hereafter, an example explains this invention. The various characteristics of the hardenability silicone composition and the hardened material were measured by the method shown below.

[0038]

[Viscosity] It measured on condition of for 25 ** and 2.5/of number of rotations using :E type viscosity meter (the product made by TOKIMEC, a DIGITAL VISCOMETER DV-U-E II type).

[Coefficient of thermal expansion]: After filling up with the hardenability silicone composition the metallic mold which has a cavity 4 mm in width, 15 mm in length, and 4 mm in depth and defoaming by 70mmHg, press hardening was carried out for 60 minutes on condition of 150 ** and 2.5MPa. Subsequently, the 2nd order was heated in 2-hour oven at 180 **, and the hardened material specimen was obtained. TMA (TM-9200 by vacuum science-and-engineering stock meeting incorporated company) was used, temperature up of the obtained specimen was carried out from 25 ** to 210 ** by a part for 2.5 ** of temperature-up/, and thermal expansion was measured.

[The rate of complex viscoelasticity]: After filling up with the hardenability silicone composition the metallic mold which has a cavity 10 mm in width, 50 mm in length, and 2 mm in depth and defoaming by 70mmHg, press hardening was carried out for 60 minutes on condition of 150 ** and 2.5MPa. Subsequently, the hardened material specimen heated the 2nd order in 2-hour oven at 180 ** was obtained. The rate of complex viscoelasticity in 25 ** when an ARES viscoelasticity measuring apparatus (made by Rheometric Scientific) is used and temperature up of the obtained specimen is carried out from -50 ** to 150 ** by a part for 0.5% of torsion, pitch [of 1 Hz], and heating-rate/of 3 ** was measured.

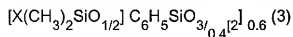
[Adhesive property] : A solder resist (the developed type solder resist of negatives, Taiyo Ink Mfg., Inc. make PSR-4000 CC02/CA-40 CC02) is applied to the base made of bismaleimide

triazine resin (common name: BT resin), ultraviolet drying -- it exposed and hardened (150 **, 1 hour), the solder resist layer (50-micrometer thickness) was formed on BT board, and this was made into adherend. In addition, the glass plate, the aluminum board, the nickel board, and the copper plate were also evaluated as adherend. After applying about 1 cm of hardenability silicone composition ³ on such adherends and heating it in 2-hour oven at 125 **, oven heating was performed at 180 ** for 2 hours, and the specimen for adhesive evaluation was obtained. From the obtained specimen, visual observation of peel-off and its adhesive property was carried out for the hardened material under the microscope using the dental spatula. The case of ** and interfacial peeling was made into x for the case where interfacial peeling of the case of cohesive failure is carried out after O and a pellicle have remained. [Hardenability examination]: The 40-micrometer-thick tape was stuck five sheets on the glass plate, the cavity (15 mm in width, 50 mm in length, and 0.2 mm in thickness) was provided, and it was used and filled up with the hardenability silicone composition for the squeegee. The obtained specimen was put into 150 ** hot wind circle method oven, the dental spatula described the hardenability silicone composition surface every 15 minutes, and time until the cobwebbing of a sample is lost was pursued.

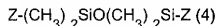
[Weight average molecular weight]: The weight average molecular weight which measured toluene by the solvent and GPC and which carried out polystyrene conversion is shown. [0039]

[Example 1]

The weight average molecular weight 1000, viscosity 9630 mPa-s which are expressed with the following siloxane-units type (3), They are 13.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (3).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 25.0 weight sections and the following siloxane-units type (4) in organopolysiloxane of the weight per epoxy equivalent 345. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 1.0 weight sections and 60.0 weight sections of spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) were mixed for HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd., amine-catalyst content: 40 % of the weight), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.



(X in a formula is 3-glycidoxy propyl group)



(The inside Z of a formula is 3-(m-hydroxyphenyl) propyl group)

[0040]

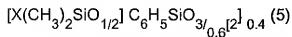
[Example 2]

The weight average molecular weight 1000, viscosity 9630 mPa-s which are expressed with said formula (3), They are 13.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (3).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 25.0 weight sections and said formula (4) in organopolysiloxane of the weight per epoxy equivalent 345. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 3-glycidoxypropyltrimetoxysilane -- 1.0 weight sections and HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections and 60.0 weight sections of spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) were mixed for 40 % of the weight, and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.

[0041]

[Example 3]

The weight average molecular weight 1000, viscosity 1290 mPa-s which are expressed with the following siloxane-units type (5), They are 17.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (5).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 21.0 weight sections and said formula (4) in organopolysiloxane of the weight per epoxy equivalent 270. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 3-glycidoxypropyltrimetoxysilane -- 1.0 weight sections and HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections were mixed for 40 % of the weight, 60.0 weight sections were mixed for spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.

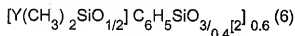


(X in a formula is 3-glycidoxy propyl group)

[0042]

[Example 4]

The weight average molecular weight 2200, viscosity 1900 mPa-s which are expressed with the following siloxane-units type (6), They are 14 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (6).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 24 weight sections and said formula (4) in organopolysiloxane of the weight per epoxy equivalent 345. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, 3-glycidioxypropyltrimetoxysilane – 1.0 weight sections and HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections and 60.0 weight sections of spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) were mixed for 40 % of the weight, and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 1.



(The inside Y of a formula is 2-(3,4-epoxycyclohexyl) ethyl group)

[0043]

[Comparative example 1]

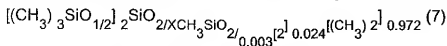
bisphenol A type liquid epoxy resin (Japan epoxy resin incorporated company make.) Epicoat 828, viscosity 15 mPa-s, and the weight per epoxy equivalent 190 23.0 weight sections, A liquefied phenol compound (made in Meiwa Chemicals, Inc., MEH8000H) 17.0 weight sections, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections and spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) 60.0 weight section were mixed for 40 % of the weight, and the hardenability epoxy resin composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 2. It was admitted that the complex modulus of the hardened material was very highly [as 2900] upright.

[0044]

[Comparative example 2]

The weight average molecular weight 45000, viscosity 17700 mPa-s which are expressed with the following siloxane-units type (7), Organopolysiloxane of the weight per epoxy equivalent 3850 36.0 weight sections, They are 2.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (7).) about organopolysiloxane of viscosity 3050 mPa-s expressed with said formula (4). The quantity from which the ratio of the

number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections were mixed for 40 % of the weight, 60.0 weight sections were mixed for spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 2.

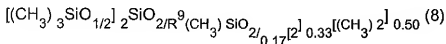


(X in a formula is 3-glycidioxy propyl group)

[0045]

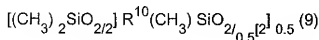
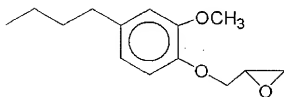
[Comparative example 3]

The weight average molecular weight 1500, viscosity 1200 mPa-s which are expressed with the following siloxane-units type (8), Organopolysiloxane of the weight per epoxy equivalent 370 21.0 weight sections, They are 17.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (8).) about organopolysiloxane of the weight average molecular weight 630 and viscosity 840 mPa-s which are expressed with the following siloxane-units type (9). The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (9) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) An encapsulation amine catalyst content 40% of the weight in bisphenol A type liquid epoxy resin 1.0 weight sections, 1.0 weight sections and spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) 70.0 weight section were mixed for 3-glycidioxypropyltrimetoxysilane, and the hardenability silicone composition was prepared. The coefficient of thermal expansion and the rate of complex viscoelasticity were investigated on condition of the above-mentioned after vacuum defoaming except having carried out oven heating at 180 ** for 2 hours, after carrying out casting to the metallic mold and carrying out oven heating at 150 ** for 2 hours. An adhesive property and cure time were investigated on condition of the above-mentioned. The characteristic is shown in Table 2.



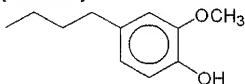
Basis as which R^9 in a formula is expressed in a lower type :

[Formula 5]



Basis as which R^{10} in a formula is expressed in a lower type :

[Formula 6]

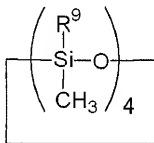


[0046]

[Comparative example 4]

The weight average molecular weight 950, viscosity 177000 mPa-s which are expressed with a lower type (10), They are 22.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (10).) about organopolysiloxane of the weight average molecular weight 630 and viscosity 840 mPa-s which are expressed with 16.0 weight sections and the above-mentioned formula (9) in organopolysiloxane of the weight per epoxy equivalent 240. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with said formula (9) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd..) An encapsulation amine catalyst content 40% of the weight in bisphenol A type liquid epoxy resin 1.0 weight sections, 1.0 weight sections and spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers) 70.0 weight section were mixed for 3-glycidoxypopyltrimetoxysilane, and the hardenability silicone composition was prepared. The coefficient of thermal expansion and the rate of complex viscoelasticity were investigated on condition of the above-mentioned after vacuum defoaming except having carried out oven heating at 180 ** for 2 hours, after carrying out casting to the metallic mold and carrying out oven heating at 150 ** for 2 hours. An adhesive property and cure time were investigated on condition of the above-mentioned. The characteristic is shown in Table 2.

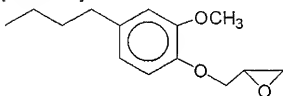
[Formula 7]



(10)

Basis as which R^9 in a formula is expressed in a lower type :

[Formula 8]

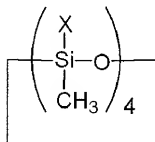


[0047]

[Comparative example 5]

The weight average molecular weight 696, viscosity 110 mPa-s which are expressed with a lower type (11), They are 20.0 weight sections (with the number of mols of the epoxy group in the organopolysiloxane expressed with a formula (11).) about organopolysiloxane of viscosity 3050 mPa-s expressed with 17.0 weight sections and said formula (4) in organopolysiloxane of the weight per epoxy equivalent 174. The quantity from which the ratio of the number of mols of the phenolic hydroxyl group in the organopolysiloxane expressed with a formula (4) is set to 1.0, as a hardening accelerator -- HX-3088 (the capsule type amine catalyst by Asahi Chemical Co., Ltd.) Amine-catalyst content: 1.0 weight sections were mixed for 40 % of the weight, 60.0 weight sections were mixed for spherical amorphous silica (ADOMA fine [made from an ADOMA, Inc. tech] ** an average of 1.5 micrometers), and the hardenability silicone composition was prepared. A coefficient of thermal expansion, the rate of complex viscoelasticity, an adhesive property, and cure time were investigated on condition of the above-mentioned after vacuum defoaming. The result is shown in Table 2.

[Formula 9]



(1 1)

(X in a formula is 3-glycidoxy propyl group)

[0048]

[Table 1]

		実施例 1	実施例 2	実施例 3	実施例 4
粘度	(Pa·s)	10	14	7	15
熱膨張率	(ppm/°C)	110	110	120	100
複素粘弾性率	(MPa)	80	86	90	90
接着性	(ソルダ―レスト)	○	○	○	○
接着性	(ニッケル)	○	○	○	○
接着性	(銅)	○	○	○	○
接着性	(アルミニウム)	○	○	○	○
接着性	(ガラス)	○	○	○	○
硬化時間	(min)	15	15	15	15

[0049]

[Table 2]

		比較例 1	比較例 2	比較例 3	比較例 4	比較例 5
粘度	(Pa·s)	199	>500	27	81	5
熱膨張率	(ppm/°C)	67	—*	130	80	120
複素粘性率	(MPa)	2900	—*	60	350	80
接着性	(ソルダレジスト)	○	×	○	○	×
接着性	(ニッケル)	○	×	○	○	×
接着性	(銅)	○	×	○	○	×
接着性	(アルミニウム)	○	×	○	○	○
接着性	(ガラス)	○	×	○	○	○
硬化時間	(min)	30	90	120	120	15

* : the hardened material was dramatically weak and was not able to measure.

[Translation done.]

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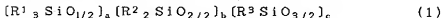
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(54) 【発明の名称】 硬化性シリコーン組成物およびその硬化物

(57) 【要約】

【課題】迅速に硬化し、硬化後は可塑性および接着性が優れた硬化樹脂となる硬化性シリコーン組成物を提供する。

【解決手段】(A) 下記シロキサン単位式(1)：



(式中、 R^1 、 R^2 、 R^3 は置換または非置換の一価炭化水素基であり、そのうち少なくとも2個は芳香環を含まないエポキシ基含有一価炭化水素基であり、 R^3 の20モル％以上はアリール基であり、 $a+b+c=1$ であり、 a は平均 $0 \leq a \leq 0.8$ であり、 b は平均 $0 \leq b \leq 0.8$ であり、 c は平均 $0.2 \leq c \leq 1.0$ である。)で表される芳香環を含まないエポキシ基含有一価炭化水素基を少なくとも2個有するオルガノポリシロキサン、

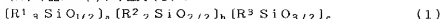
(B) フェノール性水酸基含有一価炭化水素基を少なくとも2個有する直鎖状のオルガノポリシロキサン、および(C) 硬化促進剤からなることを特徴とする、硬化性シリコーン組成物。

【選択図面】なし

【特許請求の範囲】

【請求項1】

(A) 下記シロキサン単位式 (1) :



{式中、 R^1 、 R^2 、 R^3 は置換または非置換の一端炭化水素基であり、そのうち少なくとも2個は芳香環を含まないエポキシ基含有一端炭化水素基であり、 R^3 の20モル%以上はアリール基であり、 $a+b+c=1$ であり、 a は平均 $0 \leq a \leq 0.8$ であり、 b は平均 $0 \leq b \leq 0.8$ であり、 c は平均 $0.2 \leq c \leq 1.0$ である。}

で表される芳香環を含まないエポキシ基含有一端炭化水素基を少なくとも2個有するオルガノポリシロキサン、および

(B) フェノール性水酸基含有一端炭化水素基を少なくとも2個有する直鎖状のオルガノポリシロキサン、および

(C) 硬化促進剤

からなることを特徴とする、硬化性シリコン組成物。

【請求項2】

さらに、(D) 充填剤を含有することを特徴とする請求項1記載の硬化性シリコン組成物。

【請求項3】

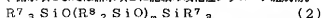
(A) 成分が液状であることを特徴とする、請求項1または請求項2に記載の硬化性シリコン組成物。

【請求項4】

(A) 成分を表すシロキサン単位式 (1) 中、 a が平均 $0 < a \leq 0.8$ であり、 b が0であることを特徴とする、請求項1または請求項2に記載の硬化性シリコン組成物。

【請求項5】

(B) 成分が、下記式 (2) で表されるオルガノポリシロキサンであることを特徴とする、請求項1または請求項2に記載の硬化性シリコン組成物。



{式中、 R^7 、 R^8 は同一または異なる置換または非置換の一端炭化水素基(但し、そのうち少なくとも2個はフェノール性水酸基含有一端炭化水素基である。)であり、 m は0~1000の整数である。}

【請求項6】

(A) 成分100重量部に対し、(B) 成分1~1000重量部と(C) 成分0.01~100重量部からなることを特徴とする、請求項1または請求項2に記載の硬化性シリコン組成物。

【請求項7】

(A) 成分のエポキシ基がグリシドキシ基あるいは、3、4-エポキシシクロヘキシル基であることを特徴とする、請求項1または請求項2に記載の硬化性シリコン組成物。

【請求項8】

液状あるいはペースト状である、請求項1または請求項2に記載の硬化性シリコン組成物。

【請求項9】

請求項1~8のいずれか1項に記載の硬化性シリコン組成物を硬化してなる硬化物。

【発明の詳細な説明】

【技術分野】

【0001】

本発明は、硬化性シリコン組成物に関し、詳しくは、硬化特性に優れ、硬化後は可撓性および接着性に優れた硬化物となる、硬化性シリコン組成物に関する。

【背景技術】

[0002]

従来、電気部品、電気・電子素子用封止材、接着剤等に使用されているエポキシ樹脂組成物などの硬化性樹脂組成物は、その硬化物の弾性率が大きく剛直であることから、硬化樹脂の熱膨張によりその樹脂で封止される電気・電子素子に大きな応力がかかる。この応力は、電気・電子素子の反りや基板の反りを引き起こしたり、硬化樹脂自体に亀裂を生じたり、あるいは電気・電子素子を破壊したり、電気・電子素子と硬化樹脂との間に隙間を生じたりする。

[0003]

硬化樹脂の低応力化を目的として、エポキシ基を有するシリコーンレジンに硬化性樹脂に配合する硬化性樹脂組成物（特開平5-295084号公報参照）、エポキシ樹脂およびシアネート樹脂とエポキシ基を有するジメチルシロキサン化合物との反応生成物からなるグアイアタッチペースト（特開平10-147764号公報、特開平10-163232号公報参照）、エポキシ基含有シリコーンオイルとフェノール系有機化合物との反応性生成物からなるグイボンディング材（特開平7-22441号公報、特開平7-118365号公報、特開平10-130465号公報参照）などが提案されている。しかし、これらの硬化物は依然として剛直で低応力化が不十分であり、電気・電子素子への適用には限界があった。

[0004]

一方、硬化性シリコーン組成物は、これを硬化して得られた硬化物が、誘電特性、体積抵抗率および絶縁破壊強度等の電気的特性に優れているため、電気部品、電気・電子素子用封止材、接着剤等に使用されている。しかし、硬化性シリコーン組成物は、これを硬化して得られた硬化物が柔軟である一方、その熱膨張率が大きかったり、強度や弾性率が低いことからその電気・電子部品の保護能力、つまり、外部からの衝撃に対する保護能力が小さかったりするという問題があった。また、硬化物の電気・電子素子に対する接着性が低いため、電気・電子素子と硬化樹脂との間に隙間を生じたりするという問題もあった。このため、充填剤を配合して柔軟な硬化物の熱膨張係数を小さくすることが考えられたが、充填剤の配合と共に弾性率が急激に大きくなり、その柔軟性や可塑性が失われるという問題があり、その改善効果にも限界があった。

[0005]

また、特開平6-306084号公報には、エポキシ変性シリコーンオイルおよびフェノール変性シリコーンオイルからなるゲル化時間の短い硬化性シリコーン樹脂組成物が提案されている。しかし、その樹脂組成物は硬化性に劣り、組成物の硬化には長い加熱時間を要するという問題点があった。

[0006]

【特許文献1】特開平5-295084号公報

【特許文献2】特開平10-147764号公報

【特許文献3】特開平10-163232号公報

【特許文献4】特開平7-22441号公報

【特許文献5】特開平7-118365号公報

【特許文献6】特開平10-130465号公報

【特許文献7】特開平6-306084号公報

【発明の開示】

【発明が解決しようとする課題】

[0007]

本発明者らは、上記問題点を解決するため鋭意努力した結果、本発明に到達した。

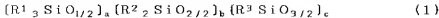
[0008]

すなわち、本発明の目的は、迅速に硬化し、硬化後は可塑性および接着性が優れた硬化樹脂となる硬化性シリコーン組成物を提供することにある。

【課題を解決するための手段】

[0009]

本発明は、(A) 下記シロキサン単位式(1)：

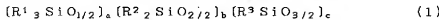


{式中、 R^1 、 R^2 、 R^3 は置換または非置換の一価炭化水素基であり、そのうち少なくとも2個は芳香環を含まないエポキシ基含有一価炭化水素基であり、 R^3 の20モル%以上はアリール基であり、 $a+b+c=1$ であり、 a は平均 $0 \leq a \leq 0.8$ であり、 b は平均 $0 \leq b \leq 0.8$ であり、 c は平均 $0.2 \leq c \leq 1.0$ である。}で表される芳香環を含まないエポキシ基含有一価炭化水素基を少なくとも2個有するオルガノポリシロキサン、(B) フェノール性水酸基含有一価炭化水素基を少なくとも2個有する直鎖状のオルガノポリシロキサン、および(C) 硬化促進剤からなることを特徴とする、硬化性シリコーン組成物に関する。

【発明の効果】

【0010】

本発明の硬化性シリコーン組成物は、(A) 下記シロキサン単位式(1)：



{式中、 R^1 、 R^2 、 R^3 は置換または非置換の一価炭化水素基であり、そのうち少なくとも2個は芳香環を含まないエポキシ基含有一価炭化水素基であり、 R^3 の20モル%以上はアリール基であり、 $a+b+c=1$ であり、 a は平均 $0 \leq a \leq 0.8$ であり、 b は平均 $0 \leq b \leq 0.8$ であり、 c は平均 $0.2 \leq c \leq 1.0$ である。}で表される芳香環を含まないエポキシ基含有一価炭化水素基を少なくとも2個有するオルガノポリシロキサン、(B) フェノール性水酸基含有一価炭化水素基を少なくとも2個有する直鎖状のオルガノポリシロキサン、および(C) 硬化促進剤からなるので、迅速に硬化し、その成形工程において加熱時間の短縮あるいは加熱硬化温度の低減が可能となる。すなわち、その成形工程において熱膨張による内部応力を小さくすることができることから、微細、脆弱な部品の保護材として使用したときその破損を防止することができるが、また基材との接着も強固となる。さらに、本発明の硬化性シリコーン組成物は、ソルダーレジスト、ニッケル、銅といった難接着性の基材に対しても良好な接着性を示す。したがって、電気部品や電子素子の封止剤、注型剤、コーティング剤、接着剤等として有用である。

【発明を実施するための最良の形態】

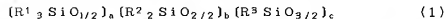
【0011】

以下、本発明の硬化性シリコーン組成物について詳細に説明する。

(A)成分は本発明組成物の主剤であり、そのエポキシ基が(B)成分中のフェノール性水酸基と反応して架橋し、硬化する。

【0012】

(A)成分は下記シロキサン単位式(1)で表されるオルガノポリシロキサンであり、 $[R^3SiO_{3/2}]$ 単位からなるか、 $[R^1_3SiO_{1/2}]$ 単位と $[R^3SiO_{3/2}]$ 単位とからなるか、 $[R^2_2SiO_{2/2}]$ 単位と $[R^3SiO_{3/2}]$ 単位とからなるか、 $[R^1_3SiO_{1/2}]$ 単位と $[R^2_2SiO_{2/2}]$ 単位と $[R^3SiO_{3/2}]$ 単位とからなり、分子構造は網状、または3次元状などである。



式中、 R^1 、 R^2 、 R^3 は置換または非置換の一価炭化水素基であり、少なくとも2個は芳香環を含まないエポキシ基含有一価炭化水素基である。エポキシ基含有一価炭化水素基中には、芳香環が含まれないことが必要である。これは、エポキシ基含有一価炭化水素基中に芳香環が含まれると本発明組成物が迅速に硬化しなくなるからである。

【0013】

芳香環を含まないエポキシ基含有一価炭化水素基以外の置換または非置換の一価炭化水素基としては、炭素原子数1~20の置換または非置換の一価炭化水素基であることが好ましく、具体的には、メチル基、エチル基、プロピル基、ブチル基、ペンチル基等のアルキル基；フェニル基、トリル基、キシリル基等のアリール基；ベンジル基、フェネチル基等のアリールアルキル基；クロロメチル基、3,3,3-トリフルオロプロピル基等のハロゲン置換アルキル基が例示される。中でも、アルキル基、特に、メチル基が好ましい。芳香環

を含まないエポキシ基含有一価炭化水素基としては、2-グリシドキシエチル基、3-グリシドキシプロピル基、4-グリシドキシブチル基、2-(3, 4-エポキシシクロヘキシル)エチル基、3-(3, 4-エポキシシクロヘキシル)プロピル基、2-(3, 4-エポキシニルボルネニル)エチル基、2-(3, 4-エポキシ-3-メチルシクロヘキシル)-2-メチルエチル基が等のエポキシ基結合アルキル基が例示される。中でも、3-グリシドキシプロピル基、2-(3, 4-エポキシシクロヘキシル)エチル基が好ましい。これらの芳香環を含まないエポキシ基含有一価炭化水素基は1分子内に2個以上存在する。(A)成分のエポキシ当量((A)成分の重量平均分子量を(A)成分1分子中のエポキシ基の数で割った数値)は、100~2000の範囲であることが好ましく、より好ましくは100~1000であり、最も好ましくは100~700である。これは、この範囲の下限未満では、本発明組成物の硬化物の可塑性が十分でなくなる場合があるからであり、この範囲の上限を超えると、本発明組成物の接着性が悪化したり、本発明組成物の硬化物が非常に脆くなったりする場合があるからである。

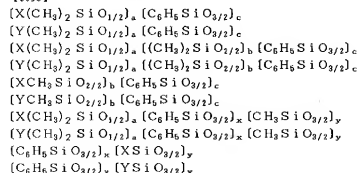
[0014]

なお、R³の20モル％以上はアリール基であり、50モル％以上がアリール基であることが好ましく、80モル％以上がアリール基であることがより好ましい。これは、上記範囲未満であると、(B)成分との相溶性や基材との接着性が十分でなかったり、本発明硬化性シリコン組成物の硬化物の強度が充分でなかったりする場合があるからである。R³のアリール基としては特にフェニル基が好ましい。a、b、cは各シリキサン単位の合計モル数を1とした場合の平均モル数を意味している。したがってa+b+c=1である。なお、a+b≠0であることが好ましい。これは、(A)成分が[R³SiO_{3/2}]単位のみからなると、その粘度が高くなりすぎ取扱い作業性が悪化する場合があるからである。aは平均0≤a≤0.8であり、好ましくは0<a≤0.6であり、より好ましくは0.3≤a≤0.6である。これは、この範囲の上限を超えるとオルガノポリシリキサンの分子量が小さくなりすぎ、本発明組成物の硬化物から(A)成分が滲み出たりして周囲を汚染したりする場合があるからである。bは平均0≤b≤0.8であり、好ましくは0≤b≤0.6である。これは、bがこの範囲の上限を超えると、本発明組成物の硬化物が脆くなる場合があるからである。cは平均0.2≤c≤1.0であり、好ましくは0.4≤c≤1.0である。これは、cがこの範囲の下限未満であると本発明組成物の接着性が十分でなくなったり、本発明硬化物が脆くなったりする場合があり、この範囲の上限を超えると粘度が高くなりすぎて本発明組成物の取扱い作業性が悪化したり、その硬化物の可塑性が適当でなくなる場合があるからである。

[0015]

シリキサン単位式(1)で表される好ましい(A)成分としては、下記式で示されるオルガノポリシリキサンが例示される。下記の各式中、a、bおよびcは前記のとおりであるが、aおよびbは0ではない、x、yは0.2≤x<1.0、0<y<0.2であり、x+y=cである。下記式中、Xはグリシドキシプロピル基、Yは2-(3, 4-エポキシシクロヘキシル)エチル基を表す。

[0016]



[0017]

(A)成分を調製する方法としては、フェニルトリアルコキシシランと芳香環を含まないエポキシ基含有一価炭化水素基を有するアルコキシシラン、例えば、3-グリシドキシプロピルトリメトキシシランや2-(3, 4-エポキシシクロヘキシル)エチルトリメトキシシランの脱アルコール縮合反応により調製する方法; フェニルトリクロロシランやフェニルトリアルコキシシランの共加水分解縮合反応により調製された分岐状フェニルオルガノシロキサン中のシラノール基と芳香環を含まないエポキシ基含有一価炭化水素基を有するアルコキシシラン、例えば、3-グリシドキシプロピルトリメトキシシランや2-(3, 4-エポキシシクロヘキシル)エチルトリメトキシシランとの脱アルコール縮合反応により調製する方法; および、フェニルトリクロロシランやフェニルトリアルコキシシランをジメチルクロロシランなどのケイ素原子結合水素原子含有シラン類存在下で共加水分解縮合反応することによって調製したケイ素原子結合水素原子含有オルガノポリシロキサンと、脂肪族不飽和基および芳香環を含まないエポキシ基含有一価炭化水素基を有する化合物とのヒドロシリル化反応により調製する方法が例示される。

【0018】

他にも、フェニルトリクロロシランやフェニルトリアルコキシシランの共加水分解縮合反応により調製された分岐状フェニルオルガノポリシロキサンを分子鎖両末端トリメチルシロキシ基封鎖メチル(3-グリシドキシプロピル)シロキサン・ジメチルシロキサン共重合体もしくは分子鎖両末端トリメチルシロキシ基封鎖メチル(2-(3, 4-エポキシシクロヘキシル)エチルシロキサン)・ジメチルシロキサン共重合体とを塩基性重合触媒の存在下で平衡重合する方法; $[C_6H_5SiO_{3/2}]$ 単位からなるシリコーンレジンと環状メチル(3-グリシドキシプロピル)シロキサンもしくは環状メチル(2-(3, 4-エポキシシクロヘキシル)エチルシロキサン)とを塩基性重合触媒の存在下で平衡重合する方法; および、 $[C_6H_5SiO_{3/2}]$ 単位からなるシリコーンレジンと環状メチル(3-グリシドキシプロピル)シロキサンもしくは環状メチル(2-(3, 4-エポキシシクロヘキシル)エチル)シロキサンと環状ジメチルシロキサンとを酸性もしくは塩基性重合触媒の存在下で平衡重合する方法も例示される。

【0019】

(A)成分は、一種類のオルガノポリシロキサンでもよく、また、二種類以上のオルガノポリシロキサンからなる混合物でもよい。25℃における性状は、液状、固体状のいずれであってもよい。固体状の場合には、有機溶剤を用いたり、加熱したりすることで、他の成分と均一に混合することができる。なお、配合や取扱いの容易さから、25℃で液体であることが好ましい。(A)成分の重量平均分子量は、500~10000が好ましく、750~3000がより好ましい。

【0020】

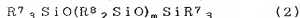
(A)成分は、その製造方法に起因する水酸基、アルコキシ基、アセトキシ基などの加水分解性基を少量含有してもよい。

【0021】

(B)フェノール性水酸基含有一価炭化水素基を少なくとも2個含有する直鎖状のオルガノポリシロキサンは、(A)成分の架橋剤であり、後述する(C)成分の作用により(A)成分中のエポキシ基と反応して本発明組成物を架橋硬化させる働きがある。(B)成分中のフェノール性水酸基含有一価炭化水素基以外の置換または非置換の一価炭化水素基としては、アルキル基、アリール基、アラルキル基、ハロゲン置換アルキル基がある。(B)成分は少数のケイ素結合水素原子、水酸基、アルコキシ基を含有してもよい。(B)成分は25℃において、固形、液状のいずれでもよいが、取扱いの容易さから、液状が好ましい。具体的には、25℃において1~1000000 mPa・sの粘度を有することが好ましく、特に、100~5000 mPa・sの範囲内であることが好ましい。これは、上記範囲の下限未満であると、本組成物を硬化して得られる硬化物の可塑性および機械的強度が低下する傾向があるからであり、一方、上記範囲の上限を超えると、本発明組成物の取扱い作業性が低下する傾向があるからである。

【0022】

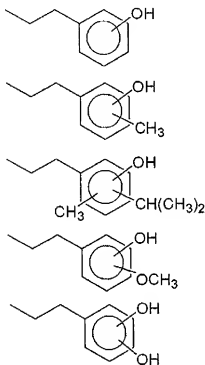
好ましい(B)成分は下記式(2)で表される。これは、本発明組成物の硬化物の可換性を向上させるのに有利となるからである。



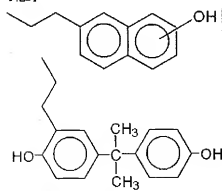
式中、 R^7 、 R^8 は同じかまたは異なる置換または非置換の一価炭化水素基であり、これらのうち少なくとも2個はフェノール性水酸基含有一価炭化水素基である。フェノール性水酸基含有一価炭化水素基は分子中に2個以上あればよいが、好ましくは2個である。好ましいフェノール性水酸基含有一価炭化水素基は、フェノール基結合アルキル基であり、下記のもの为例示される。

【0023】

【化1】



【化2】



【0024】

他の置換または非置換の一価炭化水素基としては、メチル基、エチル基、プロピル基、ブチル基、ペンチル基、ヘキシル基、ヘプチル基等のアルキル基；フェニル基、トリル基、キシリル基、ナフチル基などのアリール基；ベンジル基、フェネチル基等のアラルキル基；ビニル基、アリル基、ブテニル基、ベテニル基、ヘキセニル基などのアルケニル基；クロロメチル基、3-クロロプロピル基、3, 3, 3-トリフルオロプロピル基等のハロゲン化アルキル基が例示される。中でもアルキル基、特にメチル基が好ましい。式中の

mは0～1000の整数であり、好ましくは0～100であり、より好ましくは、0～20である。これは、式中のmが上記範囲内であると(B)成分の粘度が充分に低く、(A)成分への配合や取扱いが容易になり、さらには、本発明の硬化性シリコーン組成物を無溶剤で液状とすることが可能となるからである。

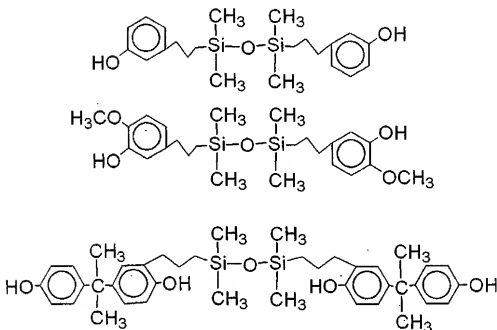
【0025】

(B)成分の配合量は、(A)成分中のエポキシ基に対して(B)成分中のフェノール性水酸基のモル比が0.2～5となる量であり、特に、0.3～2.5となる量が好ましく、0.8～1.5となる量がより好ましい。これは、(A)成分中のエポキシ基に対する(B)成分中のフェノール性水酸基のモル比が0.2未満であると組成物が十分に硬化せず、また、5を越えると硬化後の機械的特性が著しく低下するためである。

【0026】

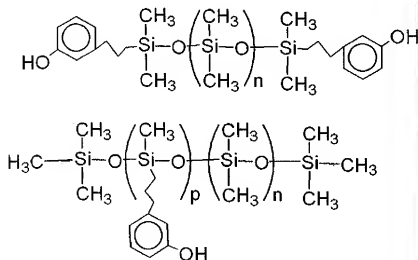
好ましい(B)成分としては、下記のものが例示される。なお、式中のnは1～20の整数であり、pは2～10の整数である。

【化3】



【0027】

【化4】



【0028】

(B)成分は、公知の方法によって調整することが出来る。例えばアルケニル基含有フェノール化合物とケイ素原子結合酸素原子を有するオルガノポリシロキサンとをヒドロシリル化触媒の存在下で付加反応させる方法が例示される。

【0029】

(C)成分は(A)成分中のエポキシ基と(B)成分中のフェノール性水酸基の反応、すなわち、本発明組成物の硬化を促進するための成分である。(C)成分としては、三級アミン化合物、アルミニウムやジルコニウム等の有機金属化合物、ホスフィン等の有機シラン化合物、異環型アミン化合物、ホウ素錯化合物、有機アンモニウム塩、有機スルホonium塩、有機過酸化化合物やこれらの反応物等が例示される。例えば、トリフェニルホスフィン、トリブチルホスフィン、トリ(p-メチルフェニル)ホスフィン、トリ(ノルフェニル)ホスフィン、トリフェニルホスフィン・トリフェニルボレート、テトラフェニルホスフィン・テトラフェニルボレート等のリン系化合物；トリエチルアミン、ベンジルジメチルアミン、 α -メチルベンジルジメチルアミン、1,8-ジアザビシクロ[5.4.0]ウンデセン7等の第3級アミン化合物；2-メチルイミダゾール、2-フェニルイミダゾール、2-フェニル-4-メチルイミダゾール等のイミダゾール化合物が例示される。なお、本発明の硬化性シリコン組成物の可使用時間を延ばすことができるので、カプセル化された硬化促進剤が好ましい。カプセル化された硬化促進剤としては、ビスフェノールA型エポキシ樹脂中にアミン触媒を配合したカプセル化アミン触媒(HX-3088；旭化成株式会社製)が挙げられる。

【0030】

(C)成分は本発明組成物を硬化させるのに十分な量であればその配合量は限定されないが、好ましくは、(A)成分100重量部当り、0.01~100重量部であり、さらに好ましくは、0.01~50重量部であり、最も好ましくは0.1~5重量部である。

【0031】

本発明組成物には、硬化物の強度を向上させるために(D)充填剤を配合してもよい。充填剤としては、ガラス繊維、アルミナ繊維、アルミナとシリカを成分とするセラミック繊維、ボロン繊維、ジルコニア繊維、炭化ケイ素繊維、金属繊維等の繊維状充填剤；溶融シリカ、結晶性シリカ、沈澱シリカ、ヒュームドシリカ、焼成シリカ、酸化亜鉛、焼成クレー、カーボンブラック、ガラスビーズ、アルミナ、タルク、炭酸カルシウム、クレー、水酸化アルミニウム、水酸化マグネシウム、硫酸バリウム、窒化アルミニウム、窒化ホウ素、炭化ケイ素、酸化アルミニウム、酸化マグネシウム、酸化チタン、酸化ベリリウム、カオリン、雲母、ジルコニア等の粉粒体状充填剤；およびこれらの2種以上の混合物が例示される。また、(D)成分の平均粒子径や形状は限定されないが、成形性が優れることから、平均粒子径が0.1~40 μ mである球状シリカが好ましい。

【0032】

(D)成分の配合量は、本発明組成物の流動性を損なわないことから(A)成分と(B)成分の合計100重量部に対して、0~2000重量部が好ましく、さらに、50~1000重量部がより好ましい。

【0033】

さらに、(A)成分または(B)成分、あるいはそれらの混合物に(D)成分を良好に分散させ、本発明組成物の硬化時の基材への接着性を向上させるために、シランカップリング剤、チタネートカップリング剤等のカップリング剤を配合してもよい。シランカップリング剤としては、3-グリシドキシプロピルトリメトキシシラン、3-グリシドキシプロピルメチルジエトキシシラン、2-(3,4-エポキシシクロヘキシル)エチルトリメトキシシラン等のエポキシ基含有アルコキシシラン；N-(2-アミノエチル)-3-アミノプロピルトリメトキシシラン、3-アミノプロピルトリエトキシシラン、N-フェニル-3-アミノプロピルトリメトキシシラン等のアミノ基含有アルコキシシラン；3-メルカプトプロピルトリメトキシシラン等のメルカプト基含有アルコキシシランが例示される。また、チタネートカップリング剤としては、i-プロポキシチタニトリ(i-イソステア

レート)が例示される。

【0034】

その他任意の成分として、テトラメトキシシラン、テトラエトキシシラン、ジメチルジメトキシシラン、メチルフェニルジメトキシシラン、メチルフェニルジエトキシシラン、フェニルトリメトキシシラン、メチルトリメトキシシラン、メチルトリエトキシシラン、ビニルトリメトキシシラン、アリルトリメトキシシラン、アリルトリエトキシシラン等のアルコキシシラン；ヘキサン、ヘプタン等の脂肪族系溶剤、トルエン、キシレン等の芳香族系溶剤、メチルエチルケトン、メチルイソブチルケトン等のケトン系溶剤等の有機溶剤を配合してもよい。

【0035】

本発明の硬化性シリコーン組成物は、(A)成分、(B)成分、(C)成分および必要により(D)成分やその他の任意成分を均一に混合することで得られる。混合方法は特に限定されないが、(A)成分、(B)成分、(C)成分、必要により(D)成分やその他の任意成分を同時に配合する方法；(A)成分と(B)成分をプレミックスした後、(C)成分と必要により(D)成分やその他の任意成分を配合する方法；(A)成分、(B)成分と必要により(D)成分やその他の任意成分をプレミックスした後、(C)成分を配合する方法が例示される。(A)成分、(B)成分、(C)成分および必要により(D)成分やその他の任意成分を混合する混合装置としては特に限定がなく、一軸または二軸の連続混合機、二本ロール、ロスミキサー、ホバートミキサー、デンタルミキサー、アラネタリミキサー、ニューグーミキサーが例示される。

【0036】

本発明の硬化性シリコーン組成物は、トランスファーモールド、インジェクションモールド、ポッティング、キャスティング、粉体塗装、浸漬塗布、滴下等の方法により使用することができ、なお、ポッティングやスクリーン印刷、塗布など種々の使用方法が選択でき、少量使用の用途にも適合しやすいことから、液状あるいはペースト状であることが好ましい。また、本発明の硬化性シリコーン組成物は、硬化後は可塑性および接着性に優れた硬化物になるので、電気部品や電子素子の封止剤、注型剤、コーティング剤、接着剤等として有用である。

【実施例】

【0037】

以下、本発明を実施例により説明する。なお、硬化性シリコーン組成物および硬化物の諸特性は以下に示す方法により測定した。

【0038】

【粘度】：E型粘度計(TOKIMEC社製、DIGITAL VISCOMETER D V-U-E II型)を用いて、25℃、回転数2.5/分の条件で測定した。

【熱膨張率】：硬化性シリコーン組成物を幅4mm、長さ15mm、深さ4mmのキャビティを有する金型に充填し、70mmHgで脱泡した後、150℃、2.5MPaの条件で60分間プレス硬化した。次いで180℃で2時間オープン中で2次加熱して硬化物試験片を得た。得られた試験片をTMA(真空理工株式会社製TM-9200)を使用して、昇温2.5℃/分で25℃から210℃まで昇温し熱膨張を測定した。

【複素粘弾性率】：硬化性シリコーン組成物を幅10mm、長さ50mm、深さ2mmのキャビティを有する金型に充填し、70mmHgで脱泡した後、150℃、2.5MPaの条件で60分間プレス硬化した。次いで180℃で2時間オープン中で2次加熱しての硬化物試験片を得た。得られた試験片をARES粘弾性測定装置(Rheometric Scientific社製)を使用し、ω=0.5%、振動数1Hz、昇温速度3℃/分で-50℃から150℃へ昇温したときの25℃での複素粘弾性率を測定した。

【接着性】：ソルダーレジスト(現象型ソルダーレジスト、太陽インキ製造株式会社製PSR-4000 C C02/C A-40 C C02)をビスマレイミド・トリアジン樹脂(通称：BT樹脂)製基盤に塗布し、紫外線乾燥、露光、硬化(150℃、1時間)して、BT基板上にソルダーレジスト層(50μm厚み)を形成し、これを被着体とした。この

他に、ガラス板、アルミ板、ニッケル板、銅板も被着体として評価した。硬化性シリコーン組成物およそ1 cm³を、これらの被着体上に塗布し125℃で2時間オープン中で加熱した後、180℃で2時間オープン加熱を行って接着性評価用試験片を得た。得られた試験片から、硬化物をデンタルスパチュラを用いて剥がし、その接着性を顕微鏡下で目視観察した。凝集破壊の場合を○、薄皮が残った状態で界面剥離する場合を△、界面剥離の場合を×、とした。

〔硬化性試験〕：ガラス板上に厚さ40 μmのテープを5枚貼り付けて幅15 mm、長さ50 mm、厚さ0.2 mmのキャビティを設け、その中に硬化性シリコーン組成物をスqueegeeを用いて充填した。得られた試験片を150℃の熱風循環式オープンに入れて、15分毎に硬化性シリコーン組成物表面をデンタルスパチュラで触れて、試料の糸引きがなくなるまでの時間を追跡した。

〔重量平均分子量〕：トルエンを溶媒としてGPCで測定した、ポリスチレン換算した重量平均分子量を示す。

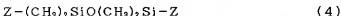
【0039】

〔実施例1〕

下記シロキサン単位式(3)で表される重量平均分子量1000、粘度9630 mPa・s、エポキシ当量345のオルガノポリシロキサンを25.0重量部、下記シロキサン単位式(4)で表される粘度3050 mPa・sのオルガノポリシロキサンを13.0重量部(式(3)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、式(4)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、HX-3088(旭化成株式会社製カプセル型アミン触媒、アミン触媒含有量：40重量%)を1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマファイン、平均1.5 μm)を60.0重量部混合して、硬化性シリコーン組成物を調製した。真空脱泡後、前述の条件で熱膨張率、複素粘弾性率、接着性、硬化時間を調べた。その結果を表1に示す。



(式中Xは、3-グリシドキシプロピル基)



(式中Zは3-(m-ヒドロキシフェニル)プロピル基)

【0040】

〔実施例2〕

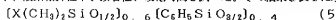
前記式(3)で表される重量平均分子量1000、粘度9630 mPa・s、エポキシ当量345のオルガノポリシロキサンを25.0重量部、前記式(4)で表される粘度3050 mPa・sのオルガノポリシロキサンを13.0重量部(式(3)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、式(4)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、3-グリシドキシプロピルトリメトキシランを1.0重量部、HX-3088(旭化成株式会社製カプセル型アミン触媒、アミン触媒含有量：40重量%)を1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマファイン、平均1.5 μm)を60.0重量部混合して、硬化性シリコーン組成物を調製した。真空脱泡後、前述の条件で熱膨張率、複素粘弾性率、接着性、硬化時間を調べた。その結果を表1に示す。

【0041】

〔実施例3〕

下記シロキサン単位式(5)で表される重量平均分子量1000、粘度1290 mPa・s、エポキシ当量270のオルガノポリシロキサンを21.0重量部、前記式(4)で表される粘度3050 mPa・sのオルガノポリシロキサンを17.0重量部(式(5)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、式(4)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、3-グリシドキシプロピルトリメトキシランを1.0重量部、HX-3088(旭化成株式会社製カプセル型アミン触媒、アミン触媒含有量：40重量%)を1.0重量部、および球状

非晶質シリカ(株式会社アドマテック製アドマファイン、平均 $1.5\mu\text{m}$)を60.0重量部を混合して、硬化性シリコン組成物を調製した。真空脱泡後、前述の条件で熱膨張率、複素粘弾性率、接着性、硬化時間を調べた。その結果を表1に示す。

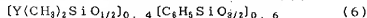


(式中Xは3-グリシドキシプロピル基)

【0042】

〔実施例4〕

下記シロキサン単位式(6)で表される重量平均分子量2200、粘度 $1900\text{mPa}\cdot\text{s}$ 、エポキシ当量345のオルガノポリシロキサンを24重量部、前記式(4)で表される粘度 $3050\text{mPa}\cdot\text{s}$ のオルガノポリシロキサンを14重量部(式(6)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、式(4)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、3-グリシドキシプロピルトリメトキシシランを1.0重量部、HX-3088(旭化成株式会社製カプセル型アミン触媒、アミン触媒含有量:40重量%)を1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマファイン、平均 $1.5\mu\text{m}$)を60.0重量部混合して、硬化性シリコン組成物を調製した。真空脱泡後、前述の条件で熱膨張率、複素粘弾性率、接着性、硬化時間を調べた。その結果を表1に示す。



(式中Yは、2-(3,4-エポキシシクロヘキシル)エチル基)

【0043】

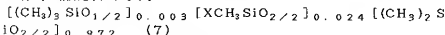
〔比較例1〕

ビスフェノールA型液状エポキシ樹脂(ジャパンエポキシレジン株式会社製、エポコート828、粘度 $15\text{mPa}\cdot\text{s}$ 、エポキシ当量190)を23.0重量部、液状フェノール化合物(明和化成株式会社製、MEH8000H)を17.0重量部、硬化促進剤としてHX-3088(旭化成株式会社製カプセル型アミン触媒、アミン触媒含有量:40重量%)を1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマファイン、平均 $1.5\mu\text{m}$)60.0重量部を混合して、硬化性エポキシ樹脂組成物を調製した。真空脱泡後、前述の条件で熱膨張率、複素粘弾性率、接着性、硬化時間を調べた。その結果を表2に示す。その硬化物の複素弾性率が2900と非常に高く剛直であることが認められた。

【0044】

〔比較例2〕

下記シロキサン単位式(7)で表される重量平均分子量45000、粘度 $17700\text{mPa}\cdot\text{s}$ 、エポキシ当量3850のオルガノポリシロキサンを36.0重量部、前記式(4)で表される粘度 $3050\text{mPa}\cdot\text{s}$ のオルガノポリシロキサンを2.0重量部(式(7)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、式(4)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、硬化促進剤としてHX-3088(旭化成株式会社製カプセル型アミン触媒、アミン触媒含有量:40重量%)を1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマファイン、平均 $1.5\mu\text{m}$)を60.0重量部を混合して、硬化性シリコン組成物を調製した。真空脱泡後、前述の条件で熱膨張率、複素粘弾性率、接着性、硬化時間を調べた。その結果を表2に示す。



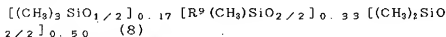
(式中Xは3-グリシドキシプロピル基)

【0045】

〔比較例3〕

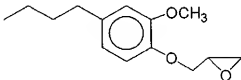
下記シロキサン単位式(8)で表される重量平均分子量1500、粘度 $1200\text{mPa}\cdot\text{s}$ 、エポキシ当量370のオルガノポリシロキサンを21.0重量部、下記シロキサン単位式(9)で表される重量平均分子量630、粘度 $840\text{mPa}\cdot\text{s}$ のオルガノポリシ

ロキサンを17.0重量部(式(8)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、式(9)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、硬化促進剤としてHX-3088(旭化成株式会社製カプセル型アミン触媒、ビスフェノールA型液状エポキシ樹脂中にカプセル化アミン触媒が4.0重量%含有)を1.0重量部、3-グリシドキシプロピルトリメトキシシランを1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマファイン、平均1.5 μ m)70.0重量部を混合して、硬化性シリコン組成物を調製した。真空脱泡後、金型に注型して150℃で2時間オープン加熱した後180℃で2時間オープン加熱した以外は、前述の条件で熱膨張率、複素粘弾性率を調べた。また、前述の条件で、接着性、硬化時間を調べた。その特性を表2に示す。

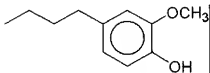


式中R⁹は、下式で表される基:

【化5】



【化6】

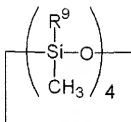


【0046】

【比較例4】

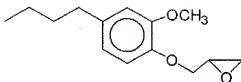
下式(10)で表される重量平均分子量950、粘度177000mPa・s、エポキシ当量240のオルガノポリシロキサンを16.0重量部、上記式(9)で表される重量平均分子量630、粘度840mPa・sのオルガノポリシロキサンを22.0重量部(式(10)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、前記式(9)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、硬化促進剤としてHX-3088(旭化成株式会社製カプセル型アミン触媒、ビスフェノールA型液状エポキシ樹脂中にカプセル化アミン触媒が4.0重量%含有)を1.0重量部、3-グリシドキシプロピルトリメトキシシランを1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマファイン、平均1.5 μ m)70.0重量部を混合して、硬化性シリコン組成物を調製した。真空脱泡後、金型に注型して150℃で2時間オープン加熱した後180℃で2時間オープン加熱した以外は、前述の条件で熱膨張率、複素粘弾性率を調べた。また、前述の条件で、接着性、硬化時間を調べた。その特性を表2に示す。

【化7】



(10)

【化8】

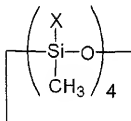


【0047】

【比較例5】

下式(11)で表される重量平均分子量696、粘度110mPa・s、エポキシ当量174のオルガノポリシロキサンを17.0重量部、前記式(4)で表される粘度3050mPa・sのオルガノポリシロキサンを20.0重量部(式(11)で表されるオルガノポリシロキサン中のエポキシ基のモル数と、式(4)で表されるオルガノポリシロキサン中のフェノール性水酸基のモル数の比が1.0となる量)、硬化促進剤としてHX-3088(旭化成株式会社製カプセル型アミン触媒、アミン酸媒含有量:40重量%)を1.0重量部、および球状非晶質シリカ(株式会社アドマテック製アドマフイン、平均1.5μm)を60.0重量部を混合して、硬化性シリコーン組成物を調製した。真空脱泡後、前述の条件で熱膨張率、複素粘弾性率、接着性、硬化時間を調べた。その結果を表2に示す。

【化9】



(11)

(式中Xは3-グリシドキシプロピル基)

【0048】

【表1】

		実施例	実施例	実施例	実施例
		1	2	3	4
粘度	(Pa·s)	10	14	7	15
熱膨張率	(ppm/°C)	110	110	120	100
複素粘弾性率	(MPa)	80	86	90	90
接着性	(ソルダーレス)	○	○	○	○
接着性	(ニッケル)	○	○	○	○
接着性	(銅)	○	○	○	○
接着性	(アルミニウム)	○	○	○	○
接着性	(ガラス)	○	○	○	○
硬化時間	(min)	15	15	15	15

【0049】

【表2】

		比較例	比較例	比較例	比較例	比較例
		1	2	3	4	5
粘度	(Pa·s)	199	>500	27	81	5
熱膨張率	(ppm/°C)	67	—*	130	80	120
複素粘弾性率	(MPa)	2900	—*	60	350	80
接着性	(ソルダーレス)	○	×	○	○	×
接着性	(ニッケル)	○	×	○	○	×
接着性	(銅)	○	×	○	○	×
接着性	(アルミニウム)	○	×	○	○	○
接着性	(ガラス)	○	×	○	○	○
硬化時間	(min)	30	90	120	120	15

*：硬化物が非常に脆く、測定できなかった。

F ターム(参考) 4J002 CD111 CP052 DA038 DA068 DE078 DE098 DE108 DE138 DE148 DE238
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EU117 EW147 EX036 EY017 FA048 FA088 FD018 FD142 FD146 FD157
FD200 GJ01 GJ02 GQ00
4J036 AK17 DA05 DC01 DC03 DC40 DC46 DD07 DD08 FA02 FA03
FA05 FA06 JA03 JA06 JA07 KA01
4J040 EC46 EK05 HA15 HA30 HA34 HA35 HD32 KA04 KA43 LA06
NA19 NA20